Homework # 10: 6.17, 6.21, 6.24, 6.27, 7.4, 7.12

6.17) What's the molecular weight?
Solution:
This is simple if you know the right equation:

$$M = \frac{RTs}{D(1 - \bar{v}\rho)}$$

$$= \frac{\left(8.314 \frac{kg \cdot m^2}{s^2 \cdot mol \cdot K}\right)(293K)(4.6 \times 10^{-13}\, s)}{\left(6.1 \times 10^{-7} \frac{cm^2}{s}\right)\left(\frac{m}{100\, cm}\right)^2 \left(1 - 0.733 \frac{cm^3}{g} \cdot 1.0 \frac{g}{cm^3}\right)}$$

$$= 68.8\, kg/mol$$

$$= 6.88 \times 10^4\, g/mol$$

6.21) *a.* Find the diameter of the protein.
Solution:
If we know the frictional coefficient, f, then we can find the radius using $f = 6\pi\eta r$. Rearranging this equation, we get

$$r = \frac{f}{6\pi\eta}$$

$$= \frac{\left(\frac{k_B T}{D}\right)}{6\pi\eta} \text{ since } f = \frac{k_B T}{D}$$

$$= \frac{\left(\frac{1.380 \times 10^{-23}\, J/K \cdot 313K}{14.25 \times 10^{-7} \frac{cm^2}{s}}\right)}{6\pi 0.0101 \frac{g}{cm \cdot s}}$$

$$= 1.59 \times 10^{-14} J \cdot s^2/g \cdot cm$$

$$= 1.59 \times 10^{-14} \frac{kg \cdot m^2}{s^2} \frac{s^2 \cdot cm}{g} \times \frac{1000g}{kg} \times \frac{100m}{cm}$$

$$= 1.59\, nm$$

This gives us the radius; the diameter is twice the radius, so $d = 3.18\, nm$.

b. Find the change in volume of the protein upon denaturation.
Solution:
Since the only thing which has changed is the diffusion constant, we can find the radius exactly as in

part a.

$$r = \frac{\left(\dfrac{k_B T}{D_{new}}\right)}{6\,\pi\,\eta}$$

$$= \frac{\left(\dfrac{1.380 \times 10^{-23}\ J/K \cdot 313K}{12.80 \times 10^{-7}\ \dfrac{cm^2}{s}}\right)}{6\,\pi\,0.0101\ \dfrac{g}{cm \cdot s}}$$

$$= 1.77\ nm$$

Since we're assuming our protein is roughly spherical, the volume is given by $\frac{4}{3}\pi r^3$, and the change in volume is

$$\Delta V = V_{new} - V_{old}$$

$$= \frac{4}{3}\pi r_{new}^3 - \frac{4}{3}\Pi r_{old}^3$$

$$= \frac{4}{3}\pi [(1.77 nm)^3 - (1.59 nm)^3]$$

$$= 6.39\ nm^3$$

c. Find the ratio of sedimentation velocities, $\dfrac{s_{high\,pH}}{s_{low\,pH}}$.

Solution:
Using the **Eqn 6.48** in the text for sedimentation, we find that

$$\frac{s_{high\,pH}}{s_{low\,pH}} = \frac{\left(\dfrac{m(1 - \bar{v}_{high} \cdot \rho)}{f_{high}}\right)}{\left(\dfrac{m(1 - \bar{v}_{low} \cdot \rho)}{f_{low}}\right)}$$

$$= \frac{f_{low}(1 - \bar{v}_{high} \cdot \rho)}{f_{high}(1 - \bar{v}_{low} \cdot \rho)}$$

$$= \frac{\left(\dfrac{k_B T}{D_{low}}(1 - \bar{v}_{high} \cdot \rho)\right)}{\left(\dfrac{k_B T}{D_{high}}(1 - \bar{v}_{low} \cdot \rho)\right)}$$

$$= \frac{D_{high}(1 - \bar{v}_{high} \cdot \rho)}{D_{low}(1 - \bar{v}_{low} \cdot \rho)} \tag{1}$$

Before we can continue this, we should determine $\bar{v}$ for both the high and low pH states. $\bar{v}$ is the partial specific volume, or the volume per gram of substance. In particular,

$$\bar{v} = (\text{volume per molecule})(\#\text{ of molecules in a mole})(\text{moles per gram}) \tag{2}$$

$$= \frac{\frac{4}{3}\pi r^3 \cdot 6.02 \times 10^{23}\frac{molecules}{moles}}{\text{molecular weight}}$$

2

So using the radius from part b. we can determine the partial specific volume.

$$\bar{v}_{high} = \frac{\frac{4}{3}\pi(1.59 \times 10^{-7}\ cm)^3 \cdot 6.02 \times 10^{23}\ \frac{1}{moles}}{14000\ \frac{g}{mol}} = 0.724\ \frac{cm^3}{g}$$

$$\bar{v}_{low} = \frac{\frac{4}{3}\pi(1.77 \times 10^{-7}\ cm)^3 \cdot 6.02 \times 10^{23}\ \frac{1}{moles}}{14000\ \frac{g}{mol}} = 0.999\ \frac{cm^3}{g}$$

We now have all the values we need to plug in to Equation (1). This gives us

$$\frac{s_{high\ pH}}{s_{low\ pH}} = \frac{14.25 \times 10^{-7}\ \frac{cm^2}{g}(1 - 0.724\frac{cm^3}{g} \cdot 1.04\frac{g}{cm^3})}{12.80 \times 10^{-7}\ \frac{cm^2}{g}(1 - 0.999\frac{cm^3}{g} \cdot 1.04\frac{g}{cm^3})} = -7.05$$

The negative number implies that the low pH (denatured) protein floats!

6.24) a. Find the molecular weight.
Solution:
We do this exactly as in problem **6.17**:

$$
\begin{aligned}
M &= \frac{RTs}{D(1 - \bar{v}\rho)} \\
&= \frac{(8.314\ \frac{kg \cdot m^2}{s^2 \cdot mol \cdot K})(293\ K)(1025 \times 10^{-13}s)}{(3.60 \times 10^{-8}\ \frac{cm^2}{s})(\frac{m}{100\ cm})^2(1 - 0.605\ \frac{cm^3}{g} \cdot 1.0\ \frac{g}{cm^3})} \\
&= 1.75 \times 10^5 \frac{kg}{mol} \\
&= 1.75 \times 10^8 \frac{g}{mol}
\end{aligned}
$$

b. Find the volume per head group.
Solution:
Recall from Eqn (2) above that the partial specific volume is equal to $\bar{v} = \dfrac{\text{volume} \cdot N_O}{MW}$. Rearranging this equation gives us:

$$
\begin{aligned}
\text{volume} &= \frac{\bar{v} \cdot MW}{N_O} \\
&= \frac{0.605\ \frac{cm^3}{g} \cdot 1.75 \times 10^8\ \frac{g}{mol}}{6.02 \times 10^{23}\ \frac{1}{mol}} \\
&= 1.76 \times 10^{-16}\ cm^3
\end{aligned}
$$

c. Find the frictional coefficient.
Solution:

$$f \ = \ \frac{k_B T}{D}$$

$$= \ \left(\frac{(1.38 \times 10^{-23} \, \frac{kg \cdot m^2}{s^2 \cdot K})(293 \, K)}{3.60 \times 10^{-8} \frac{cm^2}{s}} \right) \left(\frac{100 cm}{m} \right)^2$$

$$= \ 1.12 \times 10^{-19} \, \frac{kg}{s}$$

$$= \ 1.12 \times 10^{-6} \, \frac{g}{s}$$

d. Find the volume using the frictional coefficient.
Solution:
We know that $f = 6\pi\eta r$ (this is the Stokes equation) so we could use f above to find the radius of the head group if we actually knew the viscosity. Since that's not given, we need to hunt and peck through the book to find it: $\eta_{20,w} = 1.0050 cP$ (pg. 284). Using that, we can find the radius:

$$r \ = \ \frac{f}{6\pi\eta}$$

$$= \ \frac{1.12 \times 10^{-6} \, \frac{g}{s}}{6\pi \cdot 1.0050 \times 10^{-2} \, \frac{g}{cm \, s}}$$

$$= \ 5.91 \times 10^{-6} cm$$

Great! We now have our radius. We can transform this to volume by assuming the head group is spherical:

$$V = \frac{4}{3}\pi r^3 = 8.66 \times 10^{-16} \, cm^3 = 8.66 \times \ 10^8 \mathring{A}$$

6.27 In this problem, we denote prothombin by (P), thrombin by (T) and the cleaved peptide by (C). Find the molecular weights of P, T, and C.
Solution:
The molecular weight of P can be found using the methods from the previous problems:

$$M_P \ = \ \frac{RTs}{D(1 - \bar{v}\rho)}$$

$$= \ \frac{(8.314 \, \frac{kg \cdot m^2}{s^2 \cdot mol \cdot K})(293 \, K)(4.85 \times 10^{-13} s)}{(6.27 \times 10^{-7} \, \frac{cm^2}{s})(\frac{m}{100 \, cm})^2 (1 - 0.70 \, \frac{cm^3}{g} \cdot 1.0 \, \frac{g}{cm^3})}$$

$$= \ 63.1 \, \frac{kg}{mol}$$

$$= \ 6.31 \times 10^4 \frac{g}{mol}$$

Now we must find the molecular weights of T and C. First, note that you can write the radius in terms

of the molecular weight:

$$\begin{aligned}
V &= \frac{4}{3}\pi r^3 \quad \text{Furthermore,} \\
V &= M\bar{v}_2 \quad \text{Combining these, we find} \\
M\bar{v}_2 &= \frac{4}{3}\pi r^3 \quad \text{which rearranges to} \\
r &= \left(\frac{3M\bar{v}_2}{4\pi}\right)^{\frac{1}{3}}
\end{aligned}$$

Using this result, we can rewrite the diffusion coefficient as a function of molecular weight:

$$\begin{aligned}
D = \frac{k_B T}{f} &= \frac{k_B T}{6\pi\eta r} \\
&= \frac{k_B T}{6\pi\eta \left(\dfrac{3M\bar{v}_2}{4\pi}\right)^{\frac{1}{3}}}
\end{aligned}$$

Finally, we can look at the ratio of the diffusion constants for P and T:

$$\begin{aligned}
\frac{D_T}{D_P} &= \frac{\left(\dfrac{k_B T}{6\pi\eta_T \left(\dfrac{3M_T\bar{v}_{T2}}{4\pi}\right)^{\frac{1}{3}}}\right)}{\left(\dfrac{k_B T}{6\pi\eta_P \left(\dfrac{3M_P\bar{v}_{P2}}{4\pi}\right)^{\frac{1}{3}}}\right)} \quad \text{Since } \eta_P = \eta_T, \text{ much cancellation ensues, leaving:} \\
&= \frac{M_P^{\frac{1}{3}}\eta_T}{M_T^{\frac{1}{3}}\eta_P} \quad \text{In order to procede further, we now make the (mar-} \\
&\quad\quad\quad \text{ginally unjustified) assumption that } \eta_P = \eta_T, \text{ giving} \\
&= \left(\frac{M_P}{M_T}\right)^{\frac{1}{3}} \quad \text{So we get} \\
\left(\frac{M_T}{M_P}\right)^{\frac{1}{3}} &= \frac{D_P}{D_T} = \frac{6.24\times10^{-7}\ \frac{cm^2}{s}}{8.76\times10^{-7}\ \frac{cm^2}{s}} = 0.7123 \\
M_T &= M_P(0.7123)^3 \\
&= 2.28\times10^4\ \frac{g}{mol}
\end{aligned}$$

Only the molecular weight of C remains to be found, and since mass is conserved, we know that $M_P = M_T + M_C$. Therefore, $M_C = 6.31\times10^4\ \frac{g}{mol} - 2.28\times10^4\ \frac{g}{mol} = 4.03\times10^4\ \frac{g}{mol}$

We now forge bravely onwards to
7.4 For a reaction with mechanism

$$A \xrightarrow{k_1} B$$
$$B + C \xrightarrow{k_1} D$$
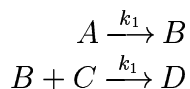
a. Write a differential equation describing the disappearance of [A].
Solution:
A differential equation relates a function to its derivatives. In this case, we know that A reacts to form B; this means that A disappears whenever B is formed. How fast does A disappear? This amount is given by k_1, the rate constant governing the reaction $A \to B$ (yes, yes, there have been Many Many uses for poor old k). The word "rate constant" means that it describes how fast the reaction occurs. The larger k_1 is, the faster A will react to form B. k_1 quantitatively describes this interaction:

$$\frac{d[A]}{dt} = -k_1[A]$$

(That's the answer to part *a.* but a little more explanation). The rate of change of [A] is $\frac{d[A]}{dt}$ if you don't understand that statement, you need to review your calculus of derivatives. Since the reaction $A \to B$ decreases the amount of A in the system, the rate of change of [A] is negative. The rate of change of [A] also depends on the amount of [A] you have. This should be unsurprising since if you didn't have any [A], you couldn't have a reaction.

b. Write a differential equation describing [B].
Solution:
B is formed by the reaction $A \to B$ but it is taken away by the reaction $B + C \to D$. This means that

$$\frac{d[B]}{dt} = k_1[A] - k_2[B][C]$$

c. Write a differential equation for the appearance of [D].
Solution:
D is formed only by $B + C \to D$.
$$\frac{d[D]}{dt} = k_2[B][C]$$

*d.* Write an equation that gives [A] at any given time.
Solution:
In order to describe the behavior of [A], we will solve the differential equation in *a.*

$$\frac{d[A]}{dt} = k_1[A] \qquad \text{We now proceed by separation of variables:}$$

$$\frac{d[A]}{[A]} = -k_1 \, dt \qquad \text{Integrate these two sides}$$

$$\ln[A] = -kt + C \qquad \text{Now exponentiate}$$

$$[A] = e^{-k_1 t}e^c$$

Almost there! Now we apply our initial conditions: We know that when $t = 0$, $[A] = [A]_0$. So:

$$
\begin{aligned}
[A] = [A]_0 &= e^{-k_1 \times 0} e^c \\
&= 1 \cdot e^c \text{ This implies that :} \\
e^c &= [A]_0 \text{ So the final equation is:} \\
[A] &= [A]_0 e^{-k_1 t}
\end{aligned}
$$

7.12a. For the reaction $A + B \to P$, derive an expression for the velocity, given that the proposed mechanism is:

$$
2A \overset{K_1}{\rightleftharpoons} A_2
$$
$$
A + B \overset{K_2}{\rightleftharpoons} C
$$
$$
A_2 + C \xrightarrow{k_3} P + 2A
$$
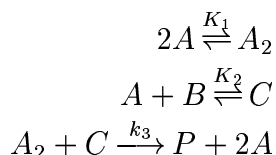
Solution:
The fact that the first two reactions proceed quickly to equilibrium means that we can approximate the concentrations of our reactants using the equilibrium constant. *Important Note: The fact that they use K_1, a capital K, denotes that they are giving you an equilibrium constant, not a rate constant, which would be given by k_1, a lower case k.* From our two equilbrium reactions, we can get the following equations:

$$
K_1 = \frac{[A_2]}{[A]^2} \tag{3}
$$

$$
K_2 = \frac{[C]}{[A][B]} \tag{4}
$$

The velocity of our reaction is equal to:

$$
v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt}
$$

The minus signs on the derivatives of $[A]$ and $[B]$ indicate that A and B are being consumed in the reaction and the positive sign of $\dfrac{d[P]}{dt}$ shows that P is being created by the reaction. In order to find the velocity, we need only choose one of these derivatives and apply the analysis we did in **7.4** to that derivative. It doesn't matter which one we pick; as an exercise, you can show that you get the same answer regardless of which derivative you pick. However, with an eye towards laziness (which is, believe it or not, one of the Great Virtues), we note that P appears only in the last reaction, whereas A appears in them all. So, eyeing our mechanism, we do the following:

$$
\begin{aligned}
\frac{d[P]}{dt} &= k_3[A_2][C] \quad \text{solve for these quantities in (3) and (4) from above, and plug in:} \\
&= k_3(K_1[A]^2)(K_2[A][B]) \\
&= K_1 K_2 k_3 [A]^3 [B]
\end{aligned}
$$

b. If you start with the same initial amounts of reactants, $[A]_0 = [B]_0$,

(i) Find v_0 if the initial amounts of $[A]$ and $[B]$ are doubled.

Solution:

We just derived an equation for v above. With our original amounts of $[A]_0$ and $[B]_0$, we can find that our initial v_0 is:

$$v_0 = K_1 K_2 k_3 [A]_0^3 [B]_0$$

We indicate the velocity which starts with double the amounts of reactants with a prime:

$$
\begin{aligned}
v_0' &= K_1 K_2 k_3 (2[A]_0)^3 (2[B]_0) \\
&= 2^4 K_1 K_2 k_3 [A]_0^3 [B]_0 \\
&= 16 v_0
\end{aligned}
$$

So the initial rate increases by a factor of 16.

(ii) What is the effect on $t_{1/2}$ if the initial concentrations of A and B are doubled?

Solution:

The first thing we will do is derive an expression for $t_{1/2}$, the half-life of the reaction. First, we will find an expression for concentration as a function of time:

$$
\begin{aligned}
\frac{d[A]}{dt} &= -K_1 K_2 k_3 [A]^3 [B] && \text{from our expression for the velocity} \\
d[A] &= -K_1 K_2 k_3 [A]^3 [B] dt \\
&= -K_1 K_2 k_3 [A]^4 dt && \text{since } [A]_0 = [B]_0 \text{ and } A \text{ and } B \text{ decrease at the same rate} \\
\frac{d[A]}{[A]^4} &= -K_1 K_2 k_3 dt && \text{separation of variables} \\
\int \frac{d[A]}{[A]^4} &= -\int K_1 K_2 k_3 dt && \text{integrating....} \\
-\frac{1}{3[A]^3} &= -K_1 K_2 k_3 t + C \\
\frac{1}{3[A]^3} &= K_1 K_2 k_3 t + C && \text{We don't say } -C \text{ since } -C \text{ is still just a constant} && (5)
\end{aligned}
$$

Now we must determine what C, our constant of integration, is. To do this, we plug in our initial amounts at time 0 and solve for C:

$$
\begin{aligned}
\frac{1}{3[A]_0^3} &= K_1 K_2 k_3 (0) + C \\
C &= \frac{1}{3[A]_0^3}
\end{aligned}
$$

Now, the half life is the point where only half of the reactants remain. In other words, it is the point where $[A] = \frac{1}{2}[A]_0$. We can therefore find $t_{1/2}$ by plugging this value into (5), along with the value for

C:

$$\frac{1}{3(\frac{[A]_0}{2})^3} = K_1 K_2 k_3 t_{1/2} + \frac{1}{3[A]_0^3}$$

$$\frac{8}{3[A]_0^3} - \frac{1}{3[A]_0^3} = K_1 K_2 k_3 t_{1/2}$$

$$\frac{7}{3[A]_0^3} = K_1 K_2 k_3 t_{1/2}$$

$$t_{1/2} = \frac{7}{3[A]_0^3 K_1 K_2 k_3}$$

Almost done! Now that we have an expression for the half-life as a function of initial concentration, we can answer the question: what happens to the half life if we double the concentration of both A and B?

$$t'_{1/2} = \frac{7}{3(2[A]_0)^3 K_1 K_2 k_3} = \frac{7}{8 \times 3[A]_0^3 K_1 K_2 k_3} = \frac{t_{1/2}}{8}$$

Whew! So doubling the concentrations of A and B decreases the half life by 1/8!

You could alternately have used equation 7.26 from your text, but calculus is good for your soul.

(iii) Find v_0 if $[A]$ remains unchanged and $[B]$ is increased 10-fold.
Solution:
We already know v_0 from part (i) above. The new v'_0 for the increased amount of B is

$$v'_0 = K_1 K_2 k_3 [A]_0^3 (10[B]_0)$$
$$= 10 K_1 K_2 k_3 [A]_0^3 [B]_0$$
$$= 10 v_0$$

So the initial rate increases by a factor of 10. Note that this means that even though the simple equation for the reaction makes it look as if the amounts of A and B are equally important, this implies that increasing A will make the reaction go much faster than the same increase in B. This means that determining the effect of initial concentrations on rates can help you determine mechanisms!